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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

00204211.7

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
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**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

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Koninklijke Philips Electronics N.V.
5621 BA Eindhoven
NETHERLANDS

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Metal hydride battery material with high storage capacity

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Metal hydride battery material with high storage capacity

The present invention relates to a hydrogen storage material, comprising a magnesium containing intermetallic compound which can form a hydride with hydrogen. The invention also relates to an electrochemical cell comprising such hydrogen storage material.

Rechargeable batteries can be discharged and then restored to their original
5 situation for reuse. Rechargeable batteries are increasingly used in portable electronic equipment, like telephones, walkmans and computers. A known type of rechargeable battery is the so-called rechargeable metal hydride battery which has a relatively high storage capacity per unit volume. An example of such metal hydride battery is a battery comprising LaNi₅ as electrochemically active material, more specifically as a negative electrode. In the
10 discharged condition, the negative electrode comprises LaNi₅, while in the charged condition hydrogen is being absorbed by said electrode resulting in LaNi₅H₆. A disadvantage of this type of battery is the relatively low storage capacity per unit weight. The latter is caused by the high density of the metal hydride, which is about 7 g/cm³.

For some time now research has been directed to suitable metal hydrides with
15 a lower density which can act as hydrogen storage material. In theory, magnesium is very suitable for hydrogen absorption. However, the temperature at which the magnesium can be charged and discharged is 400°C. Magnesium-nickel alloys appear to be better candidates for hydrogen storage material which can be used in electrochemical cells, as these alloys can be used for hydrogen absorption at lower temperatures.

20 The use of magnesium-nickel hydride for hydrogen storage is also disclosed in JP-56114801. According to the latter publication said material can store hydrogen in a stable way at high temperatures. Although magnesium-nickel hydride can absorb a relatively large amount of hydrogen, it is as such not suitable as an electrochemically active material in an electrochemical cell. One of the reasons for this is the relatively slow kinetic of hydrogen
25 absorption and hydrogen release.

In order to improve the kinetics of hydrogen absorption and hydrogen release to a sufficient level and to restrict corrosion, the amount of nickel added to a magnesium-nickel alloy has to be so high, that only a small improvement is being obtained in comparison with the known LaNi₅ material.

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The present invention aims to provide a hydrogen storage material which can be applied in an electrochemical cell and which comprises a magnesium containing intermetallic compound which can form a hydride with hydrogen and which has a high storage capacity per unit weight.

To this end the present invention provides for a hydrogen storage material according to the preamble, which is characterized in that the intermetallic compound comprises an alloy of magnesium and a trivalent metal selected from the group of Sc, Y, La and the rare earth elements.

It appears that alloys of magnesium with one of the above trivalent metals can easily be charged and discharged with hydrogen at room temperature. Moreover, the gravitational storage capacity of alloys of magnesium and a trivalent metal selected from the group of Sc, Y, La and the rare earth elements is considerably higher than the gravitational storage capacity of LaNi_5 . As a result said alloys can advantageously be used as hydrogen storage material in an electrochemical cell. As rechargeable batteries are increasingly used in portable electronic equipment, the gravitational storage capacity is of utmost importance.

In a particular embodiment the intermetallic compound comprises an alloy selected from the group of scandium-magnesium, gadolinium-magnesium and yttrium-magnesium.

Among the above group of magnesium alloys, alloys of magnesium with the trivalent metals scandium, gadolinium and yttrium have relatively very low densities and accordingly relatively high gravitational storage capacities.

Preferably, the intermetallic compound comprises a scandium-magnesium alloy.

Scandium-magnesium alloys can reversibly absorb hydrogen at room temperature. The amount of hydrogen which can be absorbed per unit weight is such that the gravitational storage capacity shows an improvement with more than a factor 4 in comparison with the gravitational storage capacity of the known LaNi_5H_x .

RU-2072113 discloses a hydrogen-absorbing alloy of the AB_5 type, comprising lanthanum and nickel, which additionally can contain a small amount of scandium. In fact, this material is completely different from the hydrogen storage material

according to the present invention as the latter basically relates to a magnesium-scandium alloy without any lanthanum or nickel present.

Advantageously, the scandium-magnesium alloy comprises 1-50 at.% scandium and 50-99 at.% magnesium, more advantageously 15-40 at.% scandium and 60-85 at.% magnesium and preferably 30-40 at.% scandium and 60-70 at.% magnesium.

The specific amounts of the different components in the alloy are determined by weighting the kinetics and the storage capacity against each other. As mentioned in the above magnesium has a high storage capacity. The kinetics of charging and discharging the alloy can be improved by the addition of scandium.

10 Preferably, the scandium-magnesium alloy comprises $Sc_{0.35}Mg_{0.65}H_x$.

Said alloy provides for a very good balance between hydrogen storage capacity and kinetics.

In a preferred embodiment the hydrogen storage material according to the present invention comprises an amount of a catalytically active material.

15 Such catalytically active material increases the kinetics of hydrogen uptake of the hydrogen storage material.

Advantageously, the catalytically active material comprises at least one metal selected from the group consisting of palladium, platinum, cobalt, nickel, rhodium or iridium, and/or a composition of the formula DE₃, wherein D is at least one element selected from the 20 group consisting of Cr, Mo and W and E is at least one element selected from the group consisting of Ni and Co.

Preferably, the catalytically active material comprises palladium or platinum.

It has been found that the addition of, for example, only 0.6 at.% of palladium to the alloy increases the rate of hydrogen uptake with orders of magnitude. The addition of 25 1.2 at.% palladium provides for even better results in hydrogen uptake.

Furthermore, the present invention relates to an electrochemically active material, which is characterized in that the material comprises a hydrogen storage material according to the present invention as described in the above.

The hydrogen storage material according to the present invention can 30 advantageously be used in fuel cells.

The invention also relates to an electrochemical cell comprising a negative electrode. Said electrochemical cell is characterized in that the negative electrode comprises a hydrogen storage material according to the above.

The electrochemical cell preferably comprises a rechargeable battery.

Finally, the present invention relates to electronic equipment powered by at least one electrochemical cell. Said electronic equipment is characterized in that the at least one electrochemical cell is an electrochemical cell as described in the above.

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The present invention is illustrated by the following exemplary embodiment.

Exemplary embodiment 1

Thin layers of $\text{Sc}_{0.3}\text{Mg}_{0.7}$ and $\text{Sc}_{0.2}\text{Mg}_{0.8}$ respectively are electrochemically charged and discharged with hydrogen in a 1M KOH solution at room temperature. The thin layers comprise films, each having a thickness of about 200 nm. Said films are provided on a polished, quartz substrate by means of electron-beam evaporation. A top layer of palladium is provided on the respective films in order to protect the films against oxidation and to catalyze the hydrogen absorption and hydrogen release. The reference electrode is a Hg/HgO electrode.

In order to determine the amount of charge which can reversibly be taken up in the film, the discharge is being measured.

The measurements show a charge capacity of 5428 C/g for $\text{Sc}_{0.3}\text{Mg}_{0.7}$, which relates to a gravimetrical storage capacity of 1508 mAh/g. The film of $\text{Sc}_{0.2}\text{Mg}_{0.8}$ shows a charge capacity of 5948 C/g, which relates to a gravimetrical storage capacity of 1652 mAh/g. For example, LaNi_5 has a gravimetrical storage capacity of only 372 mAh/g. This means that the gravimetrical storage capacity of the scandium-magnesium alloy according to the present invention shows an improvement with more than a factor 4.

The following table shows the storage capacities of several hydrogen storage materials according to the present invention. The first two columns respectively show the hydrogen storage material in the discharged state and in the charged state. The third column refers to the mol weight of the hydrogen storage material in the discharged state, while the fourth column refers to the density of the hydrogen storage material in the discharged state. The calculated volumetrical storage capacity (VSC) and the calculated gravimetrical storage capacity (GSCc) are presented in the fifth and sixth column respectively. Finally, column seven shows the measured gravimetrical storage capacity (GSCm).

Material Discharged	Material charged	Mol weight Discharged	Density discharged	VSC Ah/l	GSCc mAh/g	GSCm mAh/g
GdMgH ₂	GdMgH ₅	183.578	4.82	2078	431	
YMgH ₂	YmgH ₅	115.233	3.11	2113	680	
YMg ₂ H ₂	YMg ₂ H ₇	139.545	2.64	2459	927	
Sc _{0.2} Mg _{0.8} H _{0.3}	Sc _{0.2} Mg _{0.8} H _{2.0}	28.76	1.99	3288	1545	1652
Sc _{0.3} Mg _{0.7} H _{0.5}	Sc _{0.3} Mg _{0.7} H _{2.0}	30.86	2.12	3193	1347	1508

The known LaNi₅ shows a gravimetical storage capacity of 367 mAh/g. All the materials of the above table show an improvement in gravimetical storage capacity in 5 comparison with LaNi₅. The measured values of the hydrogen storage materials Sc_{0.2}Mg_{0.8} and Sc_{0.3}Mg_{0.7} show an improvement in gravimetical storage capacity with more than a factor 4.

Exemplary embodiment 2

10 Preparation of the scandium-magnesium alloy

A scandium-magnesium alloy is made in bulk using a molybdenum crucible. The crucible has a height of 55 mm, a diameter of about 20 mm and a wall thickness of 1.8 mm. The magnesium is placed at the bottom of the crucible, while the heavier scandium lies on top of the magnesium. The total weight of the magnesium and scandium in the crucible is 15 5 g. When the crucible has been filled, it is sealed with a molybdenum lid.

The content of the crucible is melted at 1100°C during 6 hours. During that time, the crucible is placed in a quartz tube under an argon atmosphere. After the melting treatment, the crucible is quenched in water followed by an annealing treatment at 450°C during 2 days in order to bring the alloy in thermodynamic equilibrium. The Sc_{0.35}Mg_{0.65} 20 alloy is then converted in the γ-phase.

When the presence of e.g. palladium in the alloy is desired, Sc_{0.96}Pd_{0.04} is used as a starting material, instead of pure scandium.

After the annealing treatment the molybdenum of the crucible is mechanically removed in a turning lathe. The homogeneity of the pill is checked by measuring the top side 25 and the bottom side by XRD.

Exemplary embodiment 3

Capacity measurement of the scandium-magnesium alloy

A pressed pill with 15-30 mg $Sc_{1-x}Mg_x$ powder and 135-120 mg Ni powder is attached to a nickel holder. The pill is electrolytically charged and discharged in a 2M KOH solution against a Pt counter electrode in a compartment which is separated from the counter electrode by glass frit. A few millimeters from the pill the tip of the reference electrode (Hg/HgO) is placed. The potential difference between the pill and the reference electrode is measured. Coulomb counting is used to calculate the charge and discharge of the pill. The current intensity of charging is 350 mA/g. The current intensity of discharging is 7 to 70 mA/g (0.02C to 0.2C rate). The measurements take place at 25°C.

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Exemplary embodiment 4

Two alloy samples were prepared according to the method of exemplary embodiment 2 and measured according to exemplary embodiment 3.

The first alloy comprised a pill of 29.9 mg $Sc_{0.3}Mg_{0.65}H_x$, while the second 15 alloy comprised a pill of 14.1 mg $Sc_{0.347}Mg_{0.647}Pd_{0.006}H_x$.

The first alloy shows a gravimetical capacity of 3.5 mAh/g after several of two cycles of charging and discharging, while the second alloy, at the same conditions, shows a gravimetical capacity of 980 mAh/g.

CLAIMS:

1. Hydrogen storage material, comprising a magnesium containing intermetallic compound which can form a hydride with hydrogen, characterized in that the intermetallic compound comprises an alloy of magnesium and a trivalent metal selected from the group of Sc, Y, La and the rare earth elements.

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2. Hydrogen storage material according to claim 1, characterized in that the intermetallic compound comprises an alloy selected from the group of scandium-magnesium, gadolinium-magnesium and yttrium-magnesium.

10 3. Hydrogen storage material according to claim 1 or 2, characterized in that the intermetallic compound comprises a scandium-magnesium alloy.

4. Hydrogen storage material according to claim 3, characterized in that the scandium-magnesium alloy comprises 1-50 at.% scandium and 50-99 at.% magnesium.

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5. Hydrogen storage material according to claim 3 or 4, characterized in that the scandium-magnesium alloy comprises 15-40 at.% scandium and 60-85 at.% magnesium.

20 6. Hydrogen storage material according to claims 3-5, characterized in that the scandium-magnesium alloy comprises 30-40 at.% scandium and 60-70 at.% magnesium.

7. Hydrogen storage material according to one or more of the preceding claims, characterized in that the scandium-magnesium alloy comprises $\text{Sc}_{0.35}\text{Mg}_{0.65}\text{H}_x$.

25 8. Hydrogen storage material according to one or more of the preceding claims, characterized in that it comprises an amount of a catalytically active material.

9. Hydrogen storage material according to one or more of the preceding claims, characterized in that the catalytically active material comprises at least one metal selected

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from the group consisting of palladium, platinum, cobalt, nickel, rhodium or iridium, and/or a composition of the formula DE₃, wherein D is at least one element selected from the group consisting of Cr, Mo and W and E is at least one element selected from the group consisting of Ni and Co.

5

10. Hydrogen storage material according to one or more of the preceding claims, characterized in that the catalytically active material comprises palladium or platinum.

10 11. Electrochemically active material, characterized in that the material comprises a hydrogen storage material according to one or more of the claims 1-10.

12. Electrochemical cell at least comprising a positive electrode and a negative electrode, characterized in that the negative electrode comprises a hydrogen storage material according to one or more of the claims 1-10.

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13. Electronic equipment powered by at least one electrochemical cell, characterized in that the at least one electrochemical cell is an electrochemical cell according to claim 12.

ABSTRACT:

Disclosed is a hydrogen storage material, comprising a magnesium containing intermetallic compound which can form a hydride with hydrogen. The intermetallic compound comprises an alloy of magnesium and a trivalent metal selected from the group of Sc, Y, La and the rare earth elements. Preferably, the intermetallic compound comprises a 5 scandium-magnesium alloy. In an advantageous embodiment, the hydrogen storage material comprises also a catalytically active material.

Furthermore, an electrochemically active material, as well as an electrochemical cell comprising the above hydrogen storage material are disclosed.

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